

Compatibility of Segmented Thermoelectric Generators

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Abstract:

It is well known that power generation efficiency improves when materials with appropriate properties are combined either in a cascaded or segmented fashion across a temperature gradient. Past methods for determining materials used in segmentation were mainly concerned with materials that have the highest figure of merit in the temperature range^{1, 2}. However, the example of SiGe segmented with Bi₂Te₃ and/or various skutterudites shows a marked decline in device efficiency even though SiGe has the highest figure of merit in the temperature range. The origin of the incompatibility of SiGe with other thermoelectric materials leads to a general definition of compatibility and intrinsic efficiency. The compatibility factor derived as $s = (\sqrt{1 + ZT} - 1) / \alpha T$ is a function of only intrinsic material properties and temperature, which is represented by a ratio of current to conduction heat. For maximum efficiency the compatibility factor should not change with temperature both within a single material, and in the segmented leg as a whole. This leads to a measure of compatibility not only between segments, but also within a segment. General temperature trends show that materials are more self compatible at higher temperatures, and segmentation is more difficult across a larger ΔT . The compatibility factor can be used as a quantitative guide for deciding whether a material is better suited for segmentation or cascading. Analysis of compatibility factors and intrinsic efficiency for optimal segmentation are discussed, with intent to predict optimal material properties, temperature interfaces, and/or current/heat ratios.

Introduction

Segmented thermoelectrics are an up and coming technology which if made more efficient (~15%)³ could be commercially feasible in applications such as automotive heat reclamation and deep space power systems. Increasing the efficiency for segmented thermoelectric devices has presented a problem for some time; deciding which materials, with what properties and in what temperature ranges should be used. Ideally one would like to be able to check materials with certain interface temperatures against one another to determine whether segmentation is beneficial or even feasible. Previous methods asserted that maximizing Z was the main concern when considering segmentation compatibility^{1, 2}. However, numerical calculations and experimentation have shown that skutterudite devices segmented with any amount SiGe decrease device efficiency, even though SiGe has the highest Z value in that temperature region.

Prior methods to determine compatibility or segmentation feasibility unfortunately had mixed material terms and only used average valued material properties². Two materials in direct contact could be checked against one another, but a general framework for checking compatibility did not exist, nor did the ability to predict optimal average material properties for a prospective segment, or optimal staging. The ability to compare materials independently also meant comparison free of physical constraints such as length and area of specific portions of a thermoelectric device.

Derivation of Material Reduced Efficiency

Though the Carnot efficiency is a vital part of the efficiency calculation of a thermoelectric device, it presents a problem when trying to compute, either numerically or analytically, infinitesimal segment efficiencies. In such cases, the Carnot efficiency drops to zero, and the results become trivial. Thus one works in the

framework of reduced efficiency to avoid this problem. The efficiency is defined as the Carnot efficiency times the reduced efficiency:

$$\eta \equiv \eta_c \cdot \eta_r \quad \text{Eq- 1}$$

Where the Carnot efficiency is defined as:

$$\eta_c \equiv \frac{\Delta T}{T_H} \quad \text{Eq- 2}$$

One assumes the device has the optimal length/area ratio between the N and P legs. If one considers a device whose N and P legs have identical resistivity and thermal conductivity, and whose Seebeck coefficients are equal but of opposite sign, this effectively allows examination of the N and P legs independently. One assumes there are no radiative or convective thermal losses in the device.

Starting from the definition that efficiency is electrical output power divided by heat input power, $\eta \equiv P/Q_{in}$, it can be shown that the reduced efficiency takes the form:

$$\eta_r = \frac{1}{\eta_c} \cdot \frac{I(\alpha\Delta T - IR)}{\kappa\Delta T \frac{A}{L} - \frac{I^2 R}{2} + T_H \alpha I} \quad \text{Eq- 3}$$

This can then be re-written as:

$$\eta_r = \frac{1 - \frac{IR}{\alpha\Delta T}}{1 - \frac{IR}{2\alpha T_H} + \frac{IRZT_H}{1}} \quad \text{Eq- 4}$$

The extrinsic quantities of length and area can be removed by the following substitution:

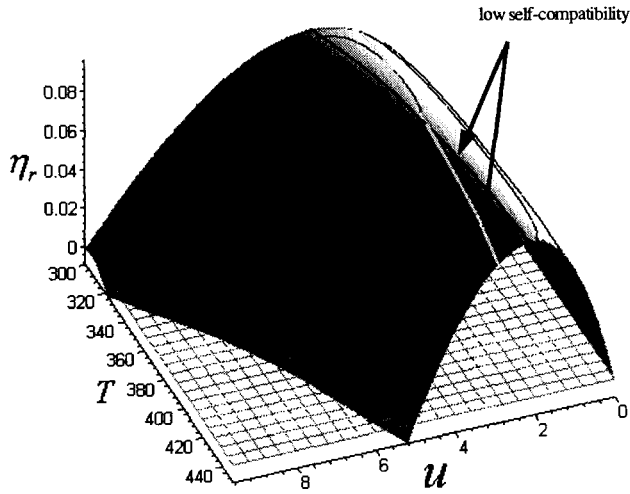


Figure 2- Reduced efficiency surface for P-Bi₂Te₃ showing optimal u value (yellow) and temperature dependent optimal u value (red).

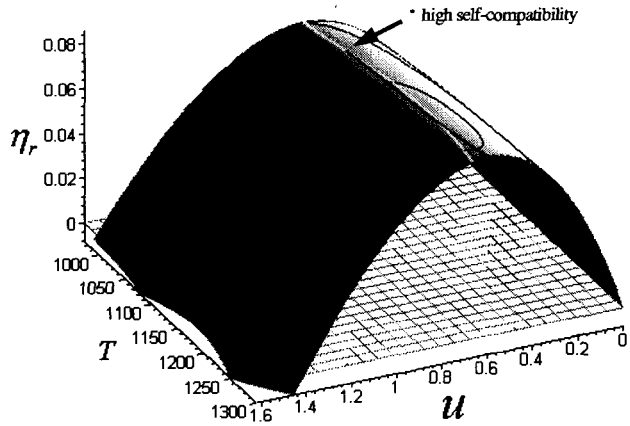


Figure 3- Reduced efficiency plot for N-SiGe showing optimal u value (yellow) and temperature dependent optimal u value (red).

Considering the compatibility condition, where material properties are now temperature dependent, it is important to realize that the compatibility of a material can change with temperature. It is possible for materials that are incompatible at the interface temperature to become compatible as one increases the hot side temperature. In the case where a material does become compatible in higher temperature regions, a material with zero resistivity, zero Seebeck coefficient, and the appropriate thermal conductivity (i.e. superconductor filler) could be used to bridge the compatibility gap between the two segments. Ideally one wants materials/segments whose optimal u values are equal through the full temperature range of the device.

When examining the device as a whole, the simplest method is to treat a segmented leg as a single material leg with discontinuous material properties. In this way one can perform the steps prescribed by equation 16 to calculate an optimal interface temperatures and u value for each leg of the device. The average u value for the whole device (both legs) is the current through the device divided by the sum of the average conduction heat through both legs, and is defined as:

$$u_{device} \equiv \left(\frac{1}{2 \cdot u_{P-leg}} + \frac{1}{2 \cdot u_{N-leg}} \right)^{-1} \quad \text{Eq- 17}$$

The case simplifies more when considering a functionally graded alloy where in essence one is performing infinite segmentation of different materials, but the material properties are fully continuous through the temperature range. Thus one can calculate an optimal u value for the graded alloy and measure self-compatibility of the alloy over the temperature range, showing that efficiency of even continuous material properties is not only dependent on Z .

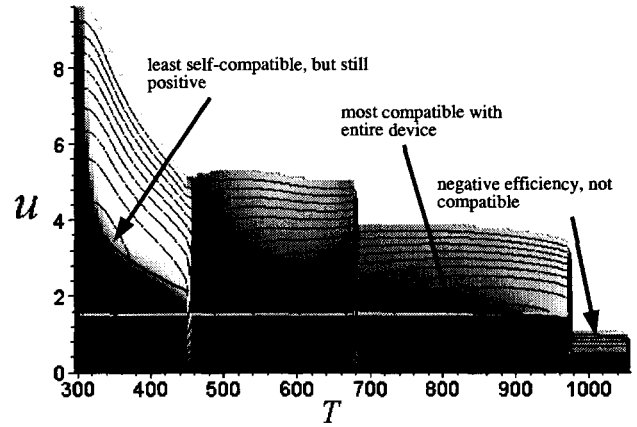


Figure 4- The reduced efficiency surface for a segmented P-leg, segment four is SiGe. u is optimized for all four segments (yellow), temperature dependent optimal values are in red.

The temperature dependent optimal u value (red line in figure 5, given by equation 12) over an entire leg brings to light some interesting points about compatibility. One starts by assuming that the thermal conductivity takes the form:

$$K = K_l + K_e \quad \text{Eq- 18}$$

Where the lattice component is assumed to be constant, and the electronic component follows the Wiedemann-Franz law:

$$K_e = \frac{LT}{\rho(T)} \quad \text{Eq- 19}$$

Thermoelectric materials, typically heavily doped, exhibit a more or less linear dependence of resistivity on temperature, giving the leading order approximation that the quantity $T/\rho(T)$ is a constant, therefore leaving the total thermal conductivity independent of temperature.

Assuming the Seebeck coefficient is a constant with temperature, and knowing that the quantity $T/\rho(T)$ and the total thermal conductivity are, to leading order, constants; the temperature dependent compatibility factor, $s(T)$, takes the form (where β is a constant):

$$s(T) = \frac{\beta}{T} \quad \text{Eq- 20}$$

$$\frac{IR}{\alpha \Delta T} = \frac{I \rho \kappa}{\kappa \Delta T \frac{A}{L} \alpha} = \frac{I}{Q_c} \cdot \frac{\rho \kappa}{\alpha} \quad \text{Eq- 5}$$

Where the conduction heat is $Q_c = \kappa \Delta T \cdot A/L$. Making the above substitution, one has:

$$\eta_r = \frac{\frac{I}{Q_c} \cdot \frac{\rho \kappa}{\alpha} \left(1 - \frac{I}{Q_c} \cdot \frac{\rho \kappa}{\alpha} \right)}{\frac{I}{Q_c} \cdot \frac{\rho \kappa}{\alpha} \left(1 - \frac{I}{Q_c} \cdot \frac{\rho \kappa}{\alpha} \cdot \frac{\Delta T}{2T_H} \right) + \frac{1}{ZT_H}} \quad \text{Eq- 6}$$

The role of $I/Q_c \cdot \rho \kappa / \alpha$ is of crucial importance to the absolute and reduced efficiencies. This quantity is composed only of intrinsic material properties, and the ratio of current to conduction heat, which is also an intrinsic property of a leg of a device. The ratio I/Q_c can be alternately thought of as the ratio of current density to heat density. Both current and conduction have the same linear dependence on length and area, thus their ratio is independent of those physical constraints. The reduced efficiency is now a function only of intrinsic material properties, temperature, and the intrinsic I/Q_c ratio. Thus given an applied voltage in any thermoelectrical system, this ratio of current to conduction heat is an intrinsic property, which describes the ratio of electron movement to phonon movement. In a real device varying the load resistance or applied voltage could change the current or current density. For ease of notation the ratio I/Q_c will be referred to as 'u.'

In the limit where ΔT is very small compared to T_H the reduced efficiency ceases to be an extrinsic quantity related to ΔT and hence length, and becomes an intrinsic quantity of the material:

$$\eta_r = \frac{u \cdot \frac{\rho \kappa}{\alpha} \left(1 - u \cdot \frac{\rho \kappa}{\alpha} \right)}{u \cdot \frac{\rho \kappa}{\alpha} + \frac{1}{ZT}} \quad \text{Eq- 7}$$

One can now plot the reduced efficiency as a function of u .

P-leg	T_c (K)	T_H (K)	s
Bi_2Te_3	300	451	2.900
Zn_4Sb_3	451	677	2.119
$\text{CeFe}_4\text{Sb}_{12}$	677	973	1.558
SiGe	973	1300	0.4116

Table 1- Temperature ranges for materials considered for segmentation in a typical P leg with their respective compatibility factors.

N-leg	T_c (K)	T_H (K)	s
Bi_2Te_3	300	433	1.624
PbTe	433	728	1.374
CoSb_3	728	973	1.093
SiGe	973	1300	0.6603

Table 2- Temperature ranges for materials considered for segmentation in a typical N leg with their respective compatibility factors.

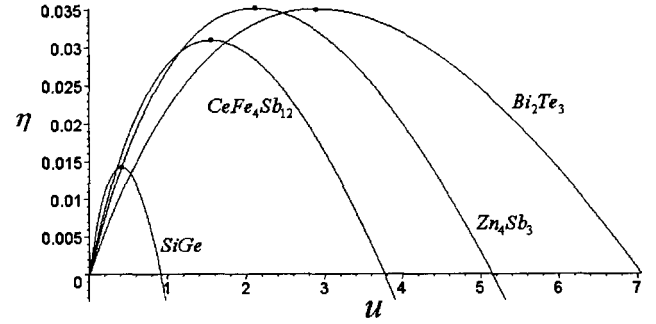


Figure 1- Plot of reduced efficiency (from equation 7) as a function of u , normalized by the Carnot efficiency, for the materials listed in Table 1. Black dots indicate maximization/compatibility factor.

The curves shown in figure 1 are analogous to curves of power versus current, where from the definition of efficiency, power and efficiency are linearly related, as well and current and u .

The compatibility factor, s , for a material is the u value that maximizes the reduced efficiency. A maximization of equation 7 yields the compatibility factor as a function of intrinsic material properties and temperature:

$$s \equiv \frac{\sqrt{1 + ZT} - 1}{\alpha T} \quad \text{Eq- 8}$$

This shows that Z is not the only concern when considering compatibility and that even temperature independent material properties are not optimal. The compatibility factor can be alternately derived from a quadratic equation using the conversation of voltage drop in the device, $\alpha \Delta T = I \cdot (R + R_L)$, assuming that the internal resistance and the load resistance have the optimal relationship that $R_L = R \sqrt{1 + ZT}$.

The crucial difference between cascading and segmentation is that the compatibility factor cannot be changed in a segmented leg. Current in the segmented device is a constant, as well as the total amount of conduction heat. Whereas in a cascaded device, the number of uncouples per stage can change, hence the conduction heat per uncouple is not fixed, as well as the ability to change current in each stage independently.

The most basic condition for compatibility between segments is that the compatibility factor, s , of the first segment lies on a positive portion of the other segment's u vs. efficiency curve. This condition, called the compatibility condition can be represented by the inequality:

$$s < u_{zero} \quad \text{Eq- 9}$$

Where u_{zero} is the non-trivial zero of equation 7, and is given by:

$$u_{zero} = \frac{\alpha}{\rho \kappa} \quad \text{Eq- 10}$$

Closer compatibility factors indicate better compatibility and higher absolute efficiency. It can be shown that the change in efficiency after adding an infinitesimal segment is:

$$\frac{d\eta}{dT} = \frac{\eta_r'(s)}{T} \quad \text{Eq- 11}$$

Where 's' is the compatibility factor of the original device and η_r' is the reduced efficiency of the new material. Thus figure 1 clearly shows how SiGe does not meet the compatibility condition with any of the other materials.

The conditions for compatibility proposed by Heikes et.al¹ considered a case where only two materials in direct electrical and thermal contact could be checked for compatibility. The method proposed by Heikes et.al leaves some ambiguity as to the change in efficiency after an infinitesimal segment of new material has been added. This method removes that ambiguity, and asserts and shows that compatibility needs to be maintained through all segments, not just segments in direct contact. Even in the basic consideration of this section, compatibility between segments is treated in a more quantitative way than Heikes et.al, who are only able to draw qualitative information about compatibility from the infinitesimal case. This method later considers transient thermoelectric properties that yield some special cases for compatibility of segments, overlooked by the non-transient method of Heikes et.al.

Optimization of Current and Conduction Heat

Knowing the temperature dependent resistivity, thermal conductivity, and Seebeck coefficient, one can plot a reduced efficiency surface for a material in a given temperature and u region. For all materials there exists a relationship between temperature and u that maximizes the reduced efficiency. Setting the partial derivative with respect to u of the temperature dependent equation 7 equal to zero, and solving for u will derive this relationship, which is the temperature dependent compatibility factor:

$$s(T) = \frac{\sqrt{1 + Z(T)T} - 1}{\alpha(T)T} \quad \text{Eq- 12}$$

The result is how the optimal u value changes with temperature, which leads to a definition of self-compatibility. When a material's optimal u value changes drastically with temperature, a segment's optimal value for a temperature range tends to lower the reduced efficiency in all but a few temperature regions within the segment. However, a material whose optimal u value remains constant with temperature has a high degree of self-compatibility; in such cases a single optimal u value is optimal for all regions. Thus one can define the optimal instantaneous self-compatibility condition as:

$$\frac{ds(T)}{dT} = 0 \quad \text{Eq- 13}$$

Over a temperature region, the self compatibility is defined as S , where a lower value indicates higher self compatibility:

$$S = \frac{\int_{T_1}^{T_2} \left| \frac{ds(T)}{dT} \right| dT}{T_2 - T_1} \quad \text{Eq- 14}$$

In practice only one u value can be chosen per leg, thus one would pick interface temperatures and a u value which maximizes all possible absolute efficiency values through all of the materials in a leg. In theory one wants to allow interface temperatures and u to vary to maximize the efficiency. If a segment is split into pieces, each with a small ΔT , one can take the integral average of the material properties over that small ΔT , substitute those values into equation 7, and multiply those reduced efficiencies by the Carnot efficiencies of those small pieces; then summing all of these small pieces one can find the approximate absolute efficiency of the segment. In the limit where the number of pieces approaches infinity and ΔT becomes dT , Harman² has shown that the efficiency of an arbitrary temperature segment is:

$$1 - \exp \left[- \int_{T_1}^{T_2} \frac{\eta_r(u, T)}{T} dT \right] = \eta(u) \quad \text{Eq- 15}$$

The efficiency is maximized when the exponent is maximized, thus if one has n segments each with a distinct reduced efficiency surface and non-optimized temperature interfaces (to prevent a trivial solution T_c and T_H are fixed), one only need solve the system of equations given by:

$$\frac{\partial}{\partial(T_i, u)} \sum_{i=1}^n \int_{T_i}^{T_{i+1}} \frac{\eta_r(u, T)}{T} dT = 0 \quad \text{Eq- 16}$$

This gives the optimal interface temperatures and u value for a leg of a device. The u value is the compatibility factor for the whole leg. This system of equations does not have analytic solutions; one must resort to numerical methods. Numerical calculations of device efficiency from this method and an accepted finite element method based on the method of Heikes et.al⁴ show a percent difference of only 0.42%. It can also be shown numerically for constant material properties that this method of efficiency calculation and the method based on:

$$\eta = \frac{\Delta T}{T_H} \cdot \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_H}$$

yield the same results.

The non-trivial zero line of the reduced efficiency surface is (from equation 10):

$$u_{zero}(T) = \frac{\alpha}{\kappa \cdot \rho(T)} \quad \text{Eq- 21}$$

This shows that the zeros and u values monotonically decrease with temperature, which lends support the notion that incompatible materials segmented at a small ΔT tend to remain incompatible (more so in most cases) with a larger ΔT . Thus an already false compatibility condition becomes more false. Statements can be made about the most general aspects of compatibility and thermoelectric performance:

Statement 1: Optimal u values tend to decrease with temperature (equation 20)

Statement 2: Materials tend to be more self-compatible at higher temperatures. (equations 13 and 20)

Statement 3: Compatibility of segments tends to decrease with increasing ΔT .

The leading order approximation lends support to the qualitative compatibility method of Heikes et.al¹, where one assumes that the qualitative compatibility behavior of an added infinitesimal segment is the same as for some arbitrary finite segment.

Cascading, Segmentation and Predicting Optimal Average Material Properties

In certain cases when a material is either barely compatible or simply incompatible with an existing segmented leg, modification to either the construction of the device or material properties may be in order.

One option is to cascade the segments in such a way that both the upper and lower stages are running at their respective optimal u values. One first assumes that the stages are running at the same current, which inherently constrains the conduction heat of the stages via u . From conservation of energy, the total conduction heat through both stages is the same, but the conduction heat per uncouple is free to change. Assuming all of this heat reaches the lower stage and is not localized, one now has an equality relationship describing the proper ratio of uncouples per stage (where primed and unprimed quantities indicate distinct stages):

$$g \cdot \left(\frac{I}{2 \cdot u_{N-leg}} + \frac{I}{2 \cdot u_{P-leg}} \right) = g' \cdot \left(\frac{I}{2 \cdot u'_{N-leg}} + \frac{I}{2 \cdot u'_{P-leg}} \right) \quad \text{Eq- 22}$$

This equation simplifies to:

$$\frac{g'}{g} = \frac{u'_{device}}{u_{device}} \quad \text{Eq- 23}$$

This can simply be called the *cascading ratio*, which pertains to any number of stages; hence one could extrapolate this method to multi-staged devices.

If the ratio of uncouples in the primed and unprimed stages is not exactly equal to the ratio g'/g , the u value for the staged device needs to be optimized. Multiplying u in the primed stage only in equation 16, by the ratio of primed and unprimed uncouples rescales the primed stage with the lower stage. One then optimizes only the u value as if all segments and stages were thermally and electrically in series (segmented), using the process described by equation 16, but holding the interfacial temperatures constant. The conduction heat through the cascaded device has not changed; hence one is actually optimizing the current.

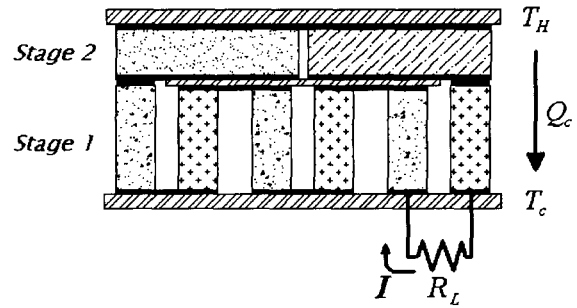


Figure 5- Resulting cascading ratio (from equation 23) for skutterudites cascaded with SiGe.

The other option is to adjust the material parameters α , κ , and ρ so that the compatibility factors are equal. Most important is to quantify the necessary change in u of the new material, if it fails the compatibility condition. This factor, which can be called the modular ratio, is found by:

$$m = \frac{s'}{s} \quad \text{Eq- 24}$$

Where s' is the value for the n^{th} segment, and s is the value for all of the segments before the n^{th} segment. The modular ratio is material scaling for the reduced efficiency (from equation 7). Multiplied by the modular ratio, the original and optimal material properties have the relationship:

$$\frac{\rho\kappa}{\alpha} \cdot m = \frac{\rho'\kappa'}{\alpha'} \quad \text{Eq- 25}$$

*where the primed material properties are allowed to vary independently

When plotted together, the absolute efficiency as a function of u for each segment in the P-leg of commonly segmented materials clearly show why SiGe is incompatible. The optimal u value for the first three segments falls on a negative portion of the SiGe efficiency curve breaking the compatibility condition. Simply adding a SiGe segment, without modification, lowers the overall efficiency of the leg, as shown in figure 6.

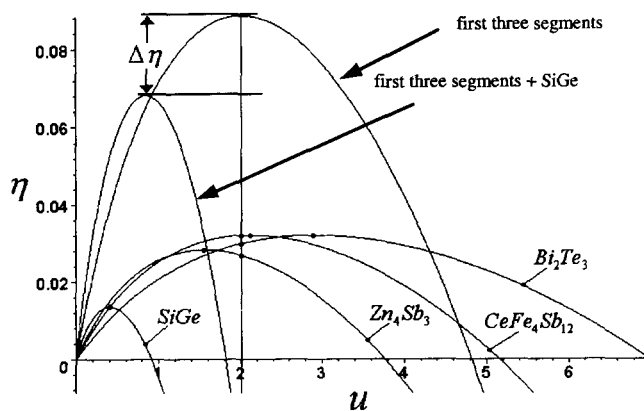


Figure 6- u vs. absolute efficiency plots: Segment 1: P-Bi₂Te₃, Segment 2: P-Zn₄Sb₃, Segment 3: P-CeFe₄Sb₁₂, Segment 4: P-SiGe

Conclusion

The intrinsic efficiency of thermoelectric generators with transient properties is defined which leads to a method for the determination of optimal interface temperatures and intrinsic ratios of current to conduction heat. The optimal conditions for segmentation and cascading are discussed, as well as optimal theoretical average material properties. The derived compatibility factor for each segment gives conditions to be met to ensure compatibility between all existing segments in a

leg. The cascading ratio of equation 23 predicts a plausible staging method for segmented skutterudites and SiGe.

Work has already begun on adapting this method to the compatibility of segmented and functionally graded alloys for use in cooling applications, where the coefficient of performance and temperature interfaces are optimized, and through a similar derivation, the reduced coefficient of performance is:

$$\phi_r = \frac{\frac{I}{Q_c} \cdot \frac{\kappa \rho}{\alpha} - \frac{1}{TZ}}{\frac{I}{Q_c} \cdot \frac{\kappa \rho}{\alpha} \left(1 + \frac{I}{Q_c} \cdot \frac{\kappa \rho}{\alpha} \right)}$$

The compatibility factor is found to be:

$$s = \frac{\sqrt{1 + ZT} + 1}{\alpha T}$$

The method of intrinsic material efficiency lends itself to multi-dimensional vector methods where material properties can be represented by tensors, and thus complete thermal and efficiency analysis is possible.

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NOMENCLATURE:

T_c	cold side temperature K	I	current A
T_H	hot side temperature K	Q_c	conduction heat W
T_i	indiced interface temperature	Q_{in}	heat input at hot junction W
R	internal resistance Ω	P	electrical power W
R_L	load resistance Ω	s	optimal u value
α	average Seebeck coefficient V/K	S	normalized self compatibility
κ	average thermal conductivity W/(m·K)	m	modular ratio
ρ	average resistivity $m\Omega \cdot cm$	n	number of segments or sub-segments per leg
Z	thermoelectric figure of merit	$u_{1 \rightarrow n-1}$	optimal value of combined segments up to $n-1$
$\alpha(T)$	temperature dependent Seebeck coefficient V/K	u_n	optimal value of n^{th} segment
$\kappa(T)$	temperature dependent thermal conductivity W/(m·K)	u_{device}	optimal value of the full segmented device
$\rho(T)$	temperature dependent resistivity $\Omega \cdot m$	u_{*leg}	optimal value of * leg of the device
$Z(T)$	temperature dependent figure of merit	κ_l	lattice component of thermal conductivity
η	absolute efficiency	κ_e	electronic component of thermal conductivity
η_c	Carnot efficiency	L	Lorenz number
η_r	reduced efficiency	g	number of uncouples per stage

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